SYSTEMATIC X-RAY STUDIES OF ELASTOMER ADDITION AGENTS

BY
ROBERT LOUIS LE TOURNEAU
B.S., Wheaton College, 1939
M.Sc., University of Akron, 1940

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Plan and Scope of the Investigation

Elastomer is a general term which includes all of the natural and synthetic rubbers. In order to make these materials into useful products it is necessary to compound them with vulcanizing agents, plasticizers and fillers. The object of this thesis is to study not only the nature of these addition agents but their effect on the elastomer and the effect of the elastomer on the addition agent. The most common elastomer is natural rubber. It is the most used in this study because of the availability of its compounds together with physical testing data for correlation and because it gives such a well defined x-ray pattern. Most of the conclusions may be carried over into the general field of elastomers. Several examples involving synthetic rubbers will be given.

The crystalline nature of stretched rubber has been known for a long time. This property of rubber is best studied by the x-ray method. Gehman[1] has recently published an extensive review paper on "The Contribution of X-ray Research to the Knowledge of Rubber." Early workers were mostly concerned with studies on pure natural rubber and many attempts were made to deduce a unit cell. Investigators still do not agree on the interpretation of the patterns in this respect. It was early shown that vulcanization did not produce any change in the diffraction pattern from rubber and it is only recently that much progress has been made in the study of compounded rubber stocks.

The degree of crystallization of the rubber in the compounded rubber stocks depends upon the stress placed upon the stock. The degree of crystallization may be quantitatively measured by the x-ray method. Crystallization on stretching has been studied for a large number of compounds under various conditions by Field.[2] That on relaxing the sample, hysteresis in the crystallization process occurs has been clearly

demonstrated by Clark.[3] The picture of what happens on stretching is this: At a given stress on the rubber sample, crystallites, oriented along the axis of stretch, begin to precipitate out of the rubber matrix. As more stress is applied, more crystals are formed. The density of the diffraction spots on the x-ray pattern increases and the density of the halo decreases. On relaxing the sample, the crystallites melt and go into solution. The diffraction spots disappear and the halo becomes more intense. The degree of crystallization is found then by comparing the density of the diffraction spots to some standard density on the film. A plot of degree of crystallization versus elongation gives the hysteresis.

The measurement of hysteresis in crystallization is the only x-ray method that allows us to follow the progress of vulcanization. One of the purposes of this study has been to investigate the entire hysteresis loop for a series of compounds containing sulfur up to eight per cent, and to investigate the effects on it of time and temperature of curing. Apparently the retraction curve is particularly sensitive to the variables mentioned. Another purpose of this investigation is to use this method of the measurement of hysteresis in crystallization to study the effect of various accelerators, alone and in combination, the effect of anti-oxidants, the effect of plasticizers and the effect of pigments such as carbon black, iron oxide, zinc oxide, lead oxide, whiting, clay, etc.

Since finely powdered crystalline inorganic fillers are now so commonly used in commercial vulcanized rubber for various purposes, we are interested in the information which may be obtained on these fillers by the x-ray diffraction method. Every x-ray pattern of vulcanized rubber compounded with fillers displays, in addition to the halo for unstretched rubber and diffraction spots for stretched rubber, diffraction rings corresponding to the various fillers in the rubber. These rings constitute the "fingerprints" by which each crystalline substance may be uniquely identified and from which its ultimate architectural plan may be deduced. If these crystalline materials have a characteristic shape, rubber, when stretched, will pull them into line. This property may readily be de-

tected in the x-ray pattern. In addition, it is possible by the x-ray method to say something about the grain size and shape of powdered crystalline materials, into which class the ordinary rubber fillers, with the possible exception of carbon black, fall.

It has been thought for a long time that certain reactions take place in the rubber matrix between accelerator and activators. Since in many cases, all of the materials involved in these reactions are crystalline at room temperature they may be positively identified in the rubber matrix by the x-ray method, and we can clearly demonstrate that reactions have taken place between two of the elastomer addition agents.

The object then of this thesis is to study by the x-ray diffraction method the various types of elastomer addition agents; namely, sulfur, accelerators, accelerator activators, finely divided crystalline fillers, and other addition agents. Not only the physical nature of the addition agents themselves is to be considered but also an explanation of their effect upon the physical behavior of the elastomer.

Apparatus and Procedures

Copper K-alpha radiation from a Philips Metalix x-ray diffraction tube was used in almost all cases. The tube was operated at 28 K.V. and 20 ma. For samples containing a large amount of iron, cobalt radiation was used. A technique was devised for taking elastomer patterns for identification of the various constituents present and a set of standard patterns made for comparison purposes. The conditions for exposure and film processing were extremely carefully controlled in the case of the patterns taken for hysteresis measurements. The photographic densities were measured on a Leeds and Northrup recording microphotometer. X-ray particle size determinations were made by the method of Clark and Rhodes.[4]

The electron microscope has been employed in conjunction with the x-ray method in the evaluation of particle size and shape of many of the elastomer addition agents. A technique was worked out for producing satisfactory dispersions of these addition agents for the ultra-microscopic examination.

Resume of Experimental Observations

1. Improvements in technique make possible complete rubber x-ray patterns for hysteresis measurements with only five minutes exposure.

2. The progress of vulcanization may be followed by x-ray hysteresis measurements of the crystallization of the rubber.

3. The extreme sensitivity of hysteresis in crystallization of rubber on stretching to changes in temperature at which the stock is investigated is demonstrated.

4. Hysteresis decreases with the time of cure for a given gum stock.

5. Crystallinity at a given elongation seems to decrease with increasing temperature of curing for equivalent cures over the range of 239-307°F.

6. For a series of gum stocks studied, at a given time and temperature of cure, the proportion of sulfur giving the greatest crystallinity at 550 per cent is between one and three per cent.

7. Inhomogeneities in the disappearance of crystallinity have been clearly demonstrated and shown to be an exaggerated localized hysteresis effect.

8. The effect of different accelerators may be studied by the x-ray hysteresis measurements of the crystallization of the rubber.

9. Reactions giving crystalline products in the rubber matrix may be studied by the x-ray method. A number of reactions between the accelerator and accelerator activator are definitely proven by this method to take place in the rubber matrix at the temperature of curing, e. g. zinc oxide plus tuads gives zimate.

10. Many of the reaction products in 9 are highly oriented in the rubber. This is suggested to be an explanation for certain desirable secondary characteristics imparted to such stocks containing higher loadings of these special accelerators.

11. Electron-microscope pictures of these highly oriented materials show them to exist as small needles which would be expected to orient easily in the rubber matrix on stretching.

12. The use of x-ray powder diffraction patterns as

"fingerprints" for identifying finely divided crystalline fillers in rubber stocks has been illustrated.

13. The determination of colloidal particle size from x-ray patterns has been illustrated for colloidal calcium carbonate of two different grades and the results correlated with physical properties of vulcanizates containing each.

14. The electron-microscope method for determining particle size and shape of rubber fillers has been illustrated for such common materials as zinc oxide and whiting.

15. It is suggested that a good criterion for reinforcing fillers is that they have the property of being oriented in the rubber matrix on stretching the rubber.

16. Orientation of a filler in the rubber matrix signifies a bond between the filler crystals and the rubber. The degree of orientation is a measure of the bonding power of the filler.

17. Hysteresis is reduced to a minimum in carbon black stocks.

18. Crystallization occurs sooner on stretching in carbon black stocks than in gum stocks.

19. Antioxidants and plasticizers do not lend themselves to study by the x-ray method.

20. Observations from x-ray patterns are given on the effect of the filler on the behavior of the rubber itself on stretching, which indicate a more profound influence than expected and give a reasonable explanation to enhanced physical properties.

References

1. Gehman, S. D.: Chem. Reviews **26**, 203 (1940).
2. Field, J. E.: J. of Applied Physics **12**, 23 (1941).
3. Clark, G. L., Kabler, M., Blaker, E., and Ball, J. M.: Ind. Eng. Chem. **32**, 1474 (1940).
4. Clark, G. L. and Rhodes, H. D.: Ind. Eng. Chem. Anal. Ed. **12**, 66 (1940).

VITA

The author was born September 12, 1918 in Portland, Oregon and received his elementary and secondary education in the public schools there. After graduation from Washington High School in 1935, he worked for one year in the refrigeration industry. In 1936 he entered Wheaton College, Wheaton, Illinois and after three years and three summers received the Bachelor of Science degree with high honors. During his last two years at Wheaton he served as an undergraduate teaching assistant in the chemistry department. In the academic year 1939-1940 he held the Firestone Fellowship in Rubber Chemistry at the University of Akron and worked in the Firestone laboratories the following summer. He received his Master of Science degree from the University of Akron. Since the fall of 1940 he has been registered in the Department of Chemistry of the Graduate School of the University of Illinois. He held a teaching assistantship in the Analytical Division until the spring of 1942 when he resigned to become an Assistant Investigator for the National Defense Research Committee.

He is a member of Wheaton College Scholastic Honor Society, Akron University Chemistry Honorary, Sigma Pi Sigma, Phi Lambda Upsilon, Sigma Xi, the American Chemical Society and Alpha Chi Sigma.

His publications are as follows:

Clark, G. L., LeTourneau, R. L., and Ball, J. M. *Rubber Chemistry and Technology 14,* 546-554 (July, 1941).

Clark, G. L. and LeTourneau, R. L. *Vanderbilt News* Vol. 11, No. 4, pages 4-11 (July-August, 1941).